

**STUDIES OF THE SUPERMOLECULAR STRUCTURE
OF CELLULOSE, ITS VARIATION WITH HISTORY,
AND ITS INFLUENCE ON FIBER PROPERTIES**

Project 3288

**Report One
A Progress Report
to**

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

April 28, 1978

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

The objective of the program undertaken in Project 3288 is to develop new methods for beneficial modification of pulp fibers. Impetus for the work came from development of new methods for monitoring changes in structure that can influence fiber properties, as well as from exploration of analogies between the behavior of cellulose and synthetic polymers. This report provides an overview of the evolution of the program since its inception and an outline of the primary concerns of our continuing effort.

The new techniques for characterization of cellulose structure are based on application of Raman spectroscopy in conjunction with x-ray diffractometry to the analysis of fiber structure. These have permitted exploration of effects of temperature and past history on the fine structure of pulp fibers. Changes in fine structure have been found to affect the properties of the fibers. Our studies have not only pointed toward new methods for beneficial modification of fiber structure, but have also resulted in a redefinition of some of the accepted notions concerning the structure of the fibers. Both of these areas will be discussed in separate reports to be issued in the near future.

Investigations of model compounds that have provided some of the background necessary for application of the new characterization techniques to cellulose are described in the Appendix.

REPORTING

This report, the first to the Membership, will provide an overview of our work in this general area since it began in 1970. Work during the first five years of the effort, much of which has been reported in separate publications, will be summarized in order to place more recent work in proper perspective. The work during the past two years will be discussed in somewhat more detail. More detailed reports on different aspects of the ongoing program will be issued in coming months.

OBJECTIVE

The broad objective of the program is to develop a rational basis for control and modification of the supermolecular structure of pulp fibers without altering the macrostructure; the principles and methods developed in this context can be readily extended to regenerated celluloses. Within this framework four general areas of activity have been defined:

1. modification of the molecular structure of fibers
2. characterization of fiber structure
3. analysis of the relative stability of cellulose polymorphs
4. the relation of molecular structure and single fiber properties
to sheet properties.

A particular emphasis for fiscal 1978 has been the search for methods for beneficial modification of kraft fibers.

INTRODUCTION

ORIGIN OF THE PROGRAM

The program was first conceived upon recognition of the fact that one of the major obstacles to deeper understanding of the properties and behavior of cellulose was that most methods available for characterizing cellulosic materials relied on solubilization or chemical decomposition prior to characterization. Methods capable of monitoring properties in a nondestructive and nonintrusive way were very limited; x-ray diffractometry and infrared spectroscopy had been applied to a limited degree. X-ray diffractometry is limited in its application to cellulose, because cellulose can be obtained only in fibrous form, and analyses of diffraction patterns from fibrous polymeric materials require the introduction of a significant number of assumptions about the structure of monomeric entities. The problems with infrared spectroscopy center about two factors. The first is that the optical heterogeneities in cellulose are such that Rayleigh scattering of electromagnetic radiation is quite high in the infrared region, so that it is difficult to record infrared spectra in which the effect of scattering can be separated from the effect of absorption. The second problem with infrared spectroscopy is that it is sensitive primarily to highly polar bonds; thus, absorption by the hydroxyl groups, the CO groups, and absorbed moisture dominate the spectra. With present instrumentation it is difficult to avoid total extinction in a number of regions of the spectrum. Thus, it is difficult to acquire information in these regions.

RAMAN SPECTROSCOPY

With the development of lasers as exciting sources, Raman spectroscopy, which is the other form of vibrational spectroscopy, experienced a significant

revival in the 1960's. The advantage of Raman spectroscopy had not been utilized before the development of the laser because most experimental systems available could not be used to record spectra from any material that had a high level of Rayleigh scattering; the intensity of Rayleigh scattered light, which is unshifted in frequency, can be greater by a factor of 10^{10} than the Raman scattered light, which is shifted in frequency and contains the information of interest. With the advent of the laser it became possible to work with low aperture double monochromators, which make possible recording of the spectra of powdered samples pressed into pellets. This led us at the Institute to assess the possibility of applying the technique to studies of cellulosic materials.

ADVANTAGES IN INVESTIGATION OF CELLULOSE

Raman spectroscopy has two significant advantages for the study of cellulosic materials. The first is that with a good spectrometer it is possible to eliminate completely the problems associated with scattering; since the radiation is shifted in frequency from that of the exciting monochromatic light, the spectrum containing information of value appears at the detector at wavelengths other than those at which Rayleigh scattering occurs. The second major advantage of Raman spectroscopy is that the Raman spectrum results from the polarizability of molecular bonds; in consequence it is most sensitive to the skeletal motions of highly covalent bonds, and least sensitive to the highly polar hydroxyl and water bonds. Its particular sensitivity to the skeletal motions provides a capability for detecting subtle changes in the shapes of complex molecules.

PROGRAM PLAN

With the above considerations in mind, the program to develop the application of Raman spectroscopy for investigating cellulosic systems was initiated at the Institute. From the outset it was recognized that because this would be a pioneering effort a substantial amount of background supportive work would be necessary. The program was structured in two parts, the first focusing on recording the Raman spectrum of varieties of cellulosic materials as well as the response of the spectra to perturbations of the structure of these cellulosic materials. The second component of the effort was focused on study of a number of model compounds; this was necessary because no prior work on carbohydrates at the level necessary to provide support for the program on cellulose had been undertaken anywhere.

Because of the nature of the two efforts it seemed logical to undertake the investigations of the cellulosic materials within the framework of an institutional research project, while undertaking the work on model compounds within the framework of the academic research program; the investigations of the model compounds lent themselves well to the format of Ph.D. research projects.

STRUCTURE MODIFICATIONS

It was in relation to the first component of the effort, that is, the component focused on cellulosic materials, that it was found desirable to seek new methods of manipulating the structure of cellulose. The basic concept was to seek an understanding of the structure of cellulose by perturbing the molecular structure and observing the response in the Raman spectrum and the x-ray diffractograms. It is out of this effort that the techniques for modifying and manipulating structure have emerged. As an understanding of the structure and of the response of

cellulosic structure to various environments were developed, they were applied in the search for methods to modify and improve the properties of cellulosic materials.

In the following section the studies of mercerization and heat treatment of fibers will be reviewed. The studies of regeneration will then be summarized. The next section of the report will be devoted to the ongoing studies of fiber modification and some related investigations. Investigations of the spectra of model compounds are outlined in the Appendix.

BACKGROUND

This section will be concerned with an overview of work completed on both cellulose and the series of classes of model compounds. Studies of native cellulose and cellulose perturbed by various treatments or by regeneration will be reviewed first.

NATIVE CELLULOSE

Fluorescence

The studies of native cellulose began with the effort to record Raman spectra of cellulose in its native state. One of the first surprises in this program was the observation that when cellulose is exposed to intense radiation from an argon ion laser, it fluoresces at a level sufficient to mask the Raman spectrum. The fluorescence was eventually traced to residues of transition metal ions retained in the cellulose; this study was the subject of the first short communication issued on this program (1). A number of procedures have been developed for treating cellulosic materials to reduce this fluorescence and to enable recording of fairly good Raman spectra from most samples of bleached cellulose. The extension to unbleached materials is currently under development with the new krypton laser which provides excitation in the red region of the spectrum; unbleached materials tend to have higher absorption in the blue and green regions, the only ones available for excitation with an argon laser.

Main Features of Raman Spectra

The most striking features of the Raman spectra of cellulosic materials recorded in the early days of the investigation were the appearance of a number of very sharp intense bands in the skeletal stretching region between 1000 and

1160 cm^{-1} and another one very intense band in the angle bending region at about 378 cm^{-1} . For such bands to be observed in a polymeric material it is necessary that there be extensive ordering with respect to at least some components of the structure. In view of the complexity of the structure of cellulose no attempt to assign the various bands were considered. Rather, the approach adopted as noted above was to attempt perturbation of the structure and explore the response of the Raman spectrum.

Effect of Mercerization on the Spectra

The first type of perturbation selected was that of mercerization. It was well known that the mercerization of cellulosic material results in conversion to an alternative polymorphic form, and it seemed plausible that one would expect a response in the spectrum reflecting the effects of polymorphic change. The first Raman spectra of mercerized materials had two surprising features. The sharp intense bands previously observed in the spectrum of native cellulose had become broadened, suggesting greater irregularity in the structure of the mercerized material. But, in addition to the broadening of some of the intense bands that remained unshifted in frequency, there was a remarkable change in the low frequency region. In this region the most intense band in the spectrum, at 378 cm^{-1} , was much reduced in intensity and appeared only as a slight shoulder on a new fairly strong peak appearing at 350 cm^{-1} . These observations, particularly the changes in the low frequency part of the spectrum, were not consistent with current theories concerning the difference between celluloses I and II. Changes in packing of the cellulose molecule in its lattice were not sufficient to explain the significant shift in frequencies in the low frequency region.

Annealing Produces Mercerized Cellulose of Higher Crystallinity

The first objective chosen after the observation of the Raman spectrum of the mercerized cellulose was to attempt to obtain cellulose II in a more crystalline form with the thought that this might reduce the width of the bands and make establishment of frequencies easier. It was noted very early in this effort that the standard mercerization procedures result in thermodynamic shock to the cellulose not unlike the quenching of molten synthetic polymers; that is, the sudden change from a strong caustic solution to the very dilute solutions resulting from the washing and neutralization would not allow time for molecular rearrangement and growth of crystalline regions. In search of more crystalline mercerized cellulose two approaches were explored. The first involved carrying out the dilution of the caustic solution over an extended period that might provide greater opportunity for molecular motion and crystallization. It was found that when the dilution of the mercerizing solution was carried out over a period of 8 hours instead of almost instantaneously, the x-ray diffractograms reflected a barely perceptible increase in order. The second approach was then introduced; this involved carrying out the slow dilution at 80°C instead of at room temperature. This approach resulted in a clearly perceptible increase in the crystallinity of the mercerized cellulose. This kind of procedure was then extended to treating the mercerized cellulose in water at 100°C and beyond that to annealing in glycerol at 150°C for varying periods. At the end of annealing periods varying from 2 days to 2 weeks it was obvious that the annealing process was resulting in substantial increase in the crystallinity of the mercerized material (2). The increased order also resulted in a sharpening of the bands in the Raman spectrum.

Annealing of Native Celluloses

The observation of the annealing effect in connection with the effort to produce mercerized cellulose of high crystallinity suggested that a similar effect

might occur in the course of treatments of native forms of cellulose at elevated temperatures. Initial explorations were carried out on cotton and kraft pulps; no perceptible changes were observed. It was soon recognized that the basic experiments on cotton and kraft pulps were not valid because those types of cellulose had been exposed to elevated temperatures for extended periods during preparation or isolation procedures. A valid test of the possibility of an annealing effect in native celluloses would require that the annealing experiment be carried out on fibers that had been pulped at low temperatures. The first attempt to anneal a low temperature pulp was with an aspen holopulp prepared at the Institute a number of years previously. This pulp was extracted with caustic solution to remove residual hemicelluloses and annealed in glycerol at 150°C. The x-ray diffractogram taken for this pulp before and after annealing reflected a significant increase in its crystallinity; the primary index used was the width at half height of the 002 diffraction peak in the diffractogram of native cellulose. This observation and similar observations on some southern pine pulps, delignified at low temperatures and extracted with caustic, set the stage for the exploration of the effect of heat treatment on papermaking properties which will be reported more comprehensively below.

Mechanism of Mercerization

Simultaneously with the above work a related thesis research project focused on the mechanism of mercerization in celluloses. This was the thesis of Bruce Dimick, on the mechanism of mercerization and the relationship between solution structure and the onset and degree of mercerization. The primary conclusion from Dimick's thesis was that the active agent in the mercerization of cellulose was the hydroxide ion in the alkali hydroxide solutions, rather than the cation as has been previously assumed by most workers. It was established that the point of onset of mercerization of very highly crystalline cellulose was the

point at which the hydroxide ions no longer had sufficient water to complete their hydration sphere. The mercerization curves for lithium hydroxide, sodium hydroxide, and potassium hydroxide were almost identical, and the small departures from identity were those expected from the limited degree of association which occurs in lithium hydroxide. The key conceptual departure in Dimick's thesis was to view the mercerization as a two-step process, the first resulting in decrystallization of the native lattice, the second involving conversion to the cellulose II lattice. In the light of later work Dimick's results suggest that the hydroxide ion was the decrystallizing agent, and the presence of water as the solvent was the key to conversion to the cellulose II lattice.

REGENERATION

Effect of DP

The regeneration studies were initially intended to explore the effects of the degree of polymerization on the level of order obtainable in the regenerated cellulose. Thus, the first studies were of regeneration from phosphoric acid solution after different periods of aging of the solutions in the acid. Prior experience at the Institute had suggested that the slow hydrolysis of the cellulose in phosphoric acid solution would make possible the attainment of varying degrees of polymerization in the 500 to 10 DP region by regeneration after periods varying from 1 to 8 weeks. This was indeed the case as demonstrated by viscosity measurements on the celluloses recovered after these periods. The first direct observations, concerned with the degree of order, suggested that the crystallinity of the regenerated cellulosic materials did increase as the degree of polymerization decreased. The effects of increased order were observed both in the x-ray diffractograms and in the Raman spectra.

Effects of Temperature: Recovery of I and IV

The experience with the effect of elevated temperatures in the annealing experiments suggested that the effect of temperature on regeneration from phosphoric acid solution should be explored; it initially appeared that it might be possible to obtain higher order at higher degrees of polymerization by regeneration at elevated temperatures. It was discovered, however, that regeneration at elevated temperatures resulted in a change in the polymorphic form recovered. Regeneration of cellulose from phosphoric acid into boiling water produced what appeared to be, on the basis of the x-ray diffractogram, a cellulose IV. This was entirely unexpected since prior reports of cellulose IV had been confined to the results of treatment of mercerized or native cellulose at temperatures between 180 and 250°C. Even more surprising was the observation that the Raman spectra of cellulose IV had features indicating that it was a mixture of molecules in the conformations prevailing in cellulose I and in cellulose II; in this respect the Raman spectrum of cellulose IV was almost indistinguishable from the Raman spectrum of a partially mercerized cellulose that would give x-ray diffractograms indicating a mixture of the polymorphs I and II. These observations led to further exploration of regeneration at even higher temperatures. Glycerol was used as the medium of regeneration, and temperatures of 120, 140, and 160°C were tried. It was found that as the temperature was increased, the proportion of molecules coming out in the I conformation increased and, under very special conditions, particularly when the degree of polymerization was rather low, the regenerated cellulose would be recovered entirely in the cellulose I conformation and produce an x-ray diffractogram and a Raman spectrum typical of an extremely crystalline native cellulose. Indeed the indications of crystallinity were higher than those of any cellulose previously observed. The recovery of cellulose in the native lattice was described in a lead report in the August 9, 1974 issue of Science (3).

Regeneration from the DMSO/PF System

Simultaneously with the studies of regeneration from phosphoric acid, Dimick, in connection with his research, explored the regeneration of cellulose from the DMSO/PF system as a function of temperature. He had initially begun his exploration in search of standards for calibration of his method of characterizing the crystallinity of cellulose. In his study he found that regeneration from the DMSO/PF system at varying temperatures resulted in the recovery of cellulose either in the II form or in the IV form, depending on the temperature at which he recovered. It was not possible to obtain cellulose in the I form from the DMSO/PF system using the materials of the relatively high degree of polymerization that he used.

New Model of Cellulose Structure

The series of studies outlined above led to proposal of the model of cellulose based on the existence of two stable conformations, represented by slight left-handed and right-handed departures from the twofold helix conformation that has been the structure accepted by some workers in the field. The model was first presented at the cellulose conference in Syracuse and is set forth in detail in the proceedings of that symposium (4), and the effects of temperature on regeneration were reported at the Centennial Symposium of the Cellulose Division of the American Chemical Society (5).

Ongoing Related Thesis Studies

Questions arising from the above studies have led to posing of the key questions that are currently under exploration in the thesis program of Jerry Ellis. This program is concerned with the influence of temperature history on the molecular conformation of cellulose.

Studies of Model Compounds

The major difficulty in interpreting the spectrum of a molecule such as cellulose is that it is made up of systems of bonds involving the same or approximately the same masses at the ends of the skeletal bonds, namely, atoms of oxygen and carbon, and that the bond energies are approximately the same for all the skeletal bonds. If one examined the frequencies of small molecule fragments one would find that the carbon-carbon and carbon-oxygen stretching vibrations when they are singly bonded are of approximately the same frequency. Yet, in spite of this, the spectra of individual carbohydrate molecules are quite distinctive; obviously the differences in conformation contribute significantly to the differences in the spectra. In order to provide the foundation for interpretation of the effect of configuration and conformation on spectra, a series of classes of model compounds were selected, and investigations of their vibrational spectra were undertaken in a systematic fashion. The scheme which is the basis for selection of model compounds and the results of the studies of their spectra are outlined in the Appendix.

ONGOING PROGRAM

The current program has a number of interrelated components focusing on pulp properties, on studies of single fibers, and on theoretical assessments of the structural model that has been developed. Each of these will be discussed in one of the following subsections of the report.

PULP PROPERTIES

Crystallization During Pulping

The studies of the effect of annealing described above led logically to the conclusions that the probability of occurrence of crystallization of the cellulosic material in cell walls during commercial pulping processes was quite high. This, then, led to the question of whether such changes can have any effect on the properties of handsheets made from commercial pulps. Therefore a series of experiments was designed to explore the effect of exposure to high temperatures on handsheet properties. The preliminary experiments involved annealing of pulps, prepared at 70°C, by immersion in glycerol and heat treatment at 170°C. In every instance there was a clear indication that handsheet properties were adversely affected. There remained some question, however, as to whether the same kinds of changes occur in aqueous media, so heat treatment in water under pressure, at 170°C was used.

Pulp Annealing Experiment

The key experiment was a fairly simple one. Loblolly pine pin chips were preextracted, delignified at 70°C using the chlorite process, and extracted with caustic to remove hemicellulose. A portion was then annealed at 170°C in water under pressure. The x-ray diffractograms revealed a much higher level of order in the annealed fibers; minor variations in the Raman spectra indicated

minimal changes in the conformation of individual cellulose chains though they reflected the changes in the crystallinity. Evaluation of papermaking characteristics showed that the annealed pulps hydrated more slowly in refinement, and that handsheets made therefrom had lower tensile, zero span, tear, and burst strength, lower tensile energy absorption and stretch, and a modulus 60-70% higher; all are consistent with increased crystallinity. Measurements of absorbency showed that annealing reduced water retention capacity to approximately 60% of its value in the unannealed pulp.

Primary Conclusion

This key experiment left little room for doubt concerning the significance of the crystallization process to the properties of commercial pulps. Indeed it suggested that the fiber properties are potentially superior to properties obtained in current commercial practice and that current commercial pulping processes develop only a fraction of the potential useful value of fibers.

Further Studies

Clearly the results of the exploratory experiments indicate that modifications of pulping processes to avoid crystallization would be desirable when the improvement in properties is needed. However, it was felt that modification of current processes was beyond the scope of the present investigation, and further effort was focused on exploring means to reverse the crystallization occurring during pulping and developing processes for recovering more of the potential of the fibers. Several approaches have been explored, with varying degrees of success. Recently a laboratory procedure has been developed which resulted in enhancement of a number of properties related to end use of the fibers. The results of these studies, together with a more detailed description of the preliminary experiments outlined above, will be the subject of the next report scheduled for release in early May.

STUDIES OF SINGLE FIBERS

Simultaneously with the effort to modify the properties of pulps the effort to extend the possibilities for characterizing fibers was continued. Among the techniques developed is one based on recording the Raman spectra of individual fibers. While Raman spectra of southern pine fibers have been recorded, because of their variability they are not well suited for use as the basis for developing new techniques. Spectra of cotton and ramie fibers have been recorded as well. Since these have been well characterized by other methods they have been chosen as the focus of work to establish the foundations of this effort.

Studies of Ramie

In the study of ramie fibers several significant observations were made. By exploiting the ability to control the polarization of the incident beam relative to the axis of the fiber and to analyze the polarization of the Raman scattered radiation, one can examine molecular orientation, as well as the degree of symmetry of the vibrations in the cellulose molecule responsible for scattering at a particular frequency. Analysis of the Raman spectra of a single ramie fiber before and after mercerization, led to the suggestion that the fundamental difference between the structures of cellulose I and cellulose II is that the native cellulose represents a right-handed departure from the twofold helix structure while the mercerized cellulose represents a left-handed departure from the twofold helix structure. The key to this conclusion was that the basic skeletal stretching vibration which produces the most intense band in the Raman spectrum of cellulose at approximately 1090 cm^{-1} undergoes a significant reduction in its degree of polarization upon mercerization of the fibers. This suggests a reduction in the symmetry of the motion involved in regeneration of this particular band. Examination of molecular models demonstrated

that rotation about the glycosidic linkage from a right-handed to a left-handed departure from the twofold helix structure does, indeed, reduce the symmetry of the particular portion of the skeletal structure which is believed responsible for the 1090 cm^{-1} band. This matter will be discussed further in the following subsection.

Comparison with Other Fibers

In the study of the Raman spectra of single fibers, comparisons were made between the spectra of ramie fibers where the molecular chains are known to be parallel to the axis of the fibers and the spectra of cotton fibers where the molecular chains are known to be at approximately 45° to the axis of the fiber. These observations suggest development of an index of molecular orientation in the fibers, based on the relative intensities of the skeletal stretching vibrations and the methine CH stretching vibrations. The relative intensities of both of these vibrations vary significantly as the plane of polarization of the incident beam is altered relative to the axis of the fiber.

Further Studies

Since the recent acquisition of an updated Raman system, it is possible to carry out quantitative studies of the spectra. The development of an index will be pursued more actively than has been possible in the past. Furthermore, it is likely that the techniques can be extended to fibers from a variety of commercial pulps. It is anticipated that with the new system it will be possible to record spectra of single fibers of southern pine pulps quite routinely.

REFINEMENT OF THEORETICAL MODELS

Relation of Polymorphy to Dimeric Models

As noted above, the earlier work has led us to the conclusion that celluloses I and II are polymorphs which have two different conformations of the

cellulose molecule, and the studies of single fibers had led to the conclusion that cellulose I represented a slightly right-handed helix while cellulose II represented a slightly left-handed helix. In further pursuit of this model the availability of information on the β -1,4 dimer of glucose was explored. It was found that, indeed, two structures had been determined using x-ray crystallography. One was the structure of cellobiose, the other was the structure of methyl cellobioside. Examining these structures, we found that the cellobiose structure represented a configuration of the glycosidic linkage similar to the one that would be observed in a slightly left-handed helix, that is, analogous to the one proposed for cellulose II. In contrast, methyl cellobioside had a configuration at the glycosidic linkage analogous to the one proposed for the slightly right-handed helix suggested for cellulose I. The contrast between these two structures became of even greater interest when it was noted that in the structure of the methyl cellobioside the intramolecular hydrogen bond involving the hydroxyl group at C-3 on one ring and the ring oxygen on the neighboring ring was in fact a bifurcated hydrogen bond in which the hydroxyl group on C-6 participated. We immediately suggested that if the spectra of cellobiose and methyl cellobioside were recorded in the OH stretching region, there should be some differences associated with the different types of intramolecular hydrogen bonds. The spectra for these two dimeric species were recorded in the OH stretching region and were found, in fact, to reflect this difference. The spectrum for cellobiose, which contains the intramolecular hydrogen bond directly to the neighboring ring oxygen, and unperturbed by participation of other groups, showed a very sharp pronounced peak superimposed on the broader continuum associated with other hydroxyl groups involved in intermolecular hydrogen bonding. In contrast, in the spectrum of methyl cellobioside, where the intramolecular hydrogen bond is significantly perturbed by the participation of C-6, the OH stretching region did not show any distinct sharp band. This comparison was then extended to celluloses I and II.

Relation to Celluloses I and II

In the OH stretching region of the infrared spectra of celluloses I and II it had been observed, as early as the work of Liang and Marchessault, that the spectrum of cellulose II contained two sharp intense bands above 3400 cm^{-1} while the spectrum of cellulose I contained only broader bands shifted to lower frequencies. This observation had not been adequately explained in any prior work. In the Raman spectra of celluloses I and II the pattern first observed by Liang and Marchessault in the infrared repeats itself. This observation, taken together with observations of the spectra of cellobiose and methyl cellobioside have led to the conclusion that, in all probability, the right-handed structure associated with cellulose I involves a bifurcated hydrogen bond analogous to the one observed in methyl cellobioside.

Some Implications

If the hypothesis that C-6 participates in the bifurcated hydrogen bond is substantiated, it could have significant implications concerning the role of C-6 in protecting glycosidic linkages from attack. Examination of three-dimensional models of the dimers suggests that if C-6 is locked into a particular conformation by its participation in the bifurcated intramolecular hydrogen bond, then the methylene hydrogens are so disposed that they would provide not only steric hindrance but also a hydrophobic environment that could interfere with molecules approaching the oxygen on the glycosidic linkages. This could, in fact, explain the much greater stability of the glycosidic linkages in cellulose when they are compared with the glycosidic linkages in xylans. Since such an effect could be important in understanding pulping mechanisms, we feel it worthy of further pursuit.

The Question of Stability

One of the outstanding questions in the effort to develop a better theoretical picture of the structure of cellulose and its unusual stability, both with respect to solubilization and with respect to melting, has been whether the stabilization originates in the pattern of hydrogen bonds, which are developed in the structure of cellulose, or whether other factors that are more entropic in nature are responsible for this stability. The different factors that might enter into this unusual stability continue under consideration.

Stability in a Model System

In one of the model systems which we have studied, an analogous question might be posed with respect to comparison of the solubilities of the scyllo- and myoinositols. Scylloinositol is the cyclohexane hexol with all six hydroxyl groups equatorial, while myoinositol has only one axial hydroxyl group, the other 5 being equatorial. Associated with this difference in configuration there is an enormous difference in solubility in water. Scylloinositol is almost insoluble in water while the myoinositol can be prepared in solutions as concentrated as 30% by weight. Clearly the difference cannot be explained on the basis of the hydrogen bonding patterns in the solid lattice because both scyllo- and myoinositols have high melting points above 300°C. The major difference between the two may be associated with the fact that scylloinositol has the possibility of hydrophilic interactions only around a perimeter which can be described as a small annular ring including the sites of hydroxyl groups, while the methine hydrogens on both sides provide a highly hydrophobic environment. In contrast, myoinositol has the hydrophobic environment on one side significantly perturbed by the one axial hydrogen. This may be sufficient to provide different interactions stabilizing the hydration of molecules.

Comparison with Hemicelluloses

It should be noted that when one compares cellulose with some of the β -1,4 linked hemicelluloses that coexist with it in the plant cell walls, one finds that the major difference is that some of the anhydropyranose units making up the hemicelluloses have an occasional axial hydroxyl group; this may provide a basis for understanding the difference in relative solubilities of the hemicelluloses and cellulose and, in a more absolute sense, the unusual stability of the structure of cellulose.

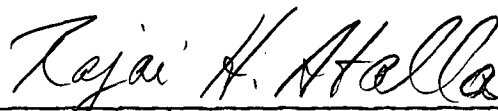
FUTURE WORK

The present phase of fiber modification studies will be concluded and reported to the membership in greater detail in a report to be issued in the near future. Emphasis will then be centered in two areas. The first will be concerned with further refinement of our characterization techniques taking full advantage of our updated Raman spectrometer system as well as a contemplated modification of the x-ray diffractometer. The second, and perhaps more important area, will be further development of our conceptual framework for interpreting the experimental observations; progress in this area is the key to developing better methods for modifying and controlling fiber structure. As the techniques for characterization and the conceptual apparatus are developed, they will be applied to explore the range of variability of fiber characteristics that may be important to end use properties. Initially, intra-species variability will be examined, and eventually the range of variability in typical commercial pulps will be explored. Finally, looking further ahead, we will undertake a preliminary assessment of the applicability of some new statistical approaches for relating fiber and network parameters to sheet properties. We believe that the availability and capabilities of modern computers make possible the application of methods of statistical modeling that might realistically approximate the relationship between fiber and network parameters and sheet properties. Such models may have been proposed in the past, but because analytical solutions were not possible for realistic models, they have not been very productive; we believe that the removal of the constraint imposed by the need for analytical solutions opens up the possibility of more successful development of useful models.

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A handwritten signature in cursive script, reading "Rajai H. Atalla". The signature is written in dark ink and is positioned above a horizontal line.

Rajai H. Atalla
Chemical Sciences Division

APPENDIX

The first three classes of model compounds investigated were the pentoses and two classes of derivatives. The 1,5-anhydropentitols were the first investigated in the thesis program of L. Pitzner. This was followed with a study of the spectra of the pentitols and erythritol in the thesis program of G. Watson. Finally, the pentoses were investigated in the thesis program of S. Edwards..

The 1,5-Anhydropentitols

The 1,5-anhydropentitols were selected for investigation as the first group because the absence of the hydroxyl group on C-1 made the half of the molecule in the immediate neighborhood of the ring oxygen symmetric, and it eliminated problems of mutarotation in examination of the spectra of the solutions. Since this was the first group investigated the objective was to find whether it would be possible to account for the spectral differences strictly in terms of the differences in geometry between the three derivatives of the pentoses examined. In order to carry out this investigation it was necessary to introduce into the methodology of the analysis of vibrational spectra nonlinear refinement procedures that had not been previously used with molecules of this size; in this respect our program here at the Institute was a pioneering effort in spectroscopy. When it was clear that it would be possible to account for the differences in the spectra of the 1,5-anhydropentitols in terms of the differences in their geometry the study was extended to the pentitols and the pentoses.

The Pentitols

The pentitols were investigated because the open chains eliminated the effect of the presence of a ring oxygen. Thus, the diversity of the bonds making up the molecules was reduced. In addition, it was desired to establish whether significant differences would arise when the spectra of open extended chain

molecules were investigated by this approach. It was established indeed that the open chain molecules were more sensitive to perturbation through hydrogen bonding with neighboring molecules and it was not possible to fit the spectra of the pentitols to the same degree as was possible with the first class of compounds.

The Pentoses

The pentoses were investigated next to explore the effect of the introduction of the anomeric hydroxyl group on the vibrational spectra. It was found possible to fit the spectra of the pentoses fairly well and indeed to use the potential constants developed in this fit to predict the spectra of some pentose derivatives. The fit to the spectra of the pentoses was better than that of the fit to the spectra of the pentitols indicating that the ring nature of the basic sugar molecules does indeed make the isolated molecule approximation a more valid one than in the case of the pentitols which are open extended chains.

The Hexoses

The next group of model compounds were the hexoses which were investigated in the thesis program of H. Wells. In this instance it was possible to secure glucose in enough isotopic variants that the fit was developed primarily for the spectra of glucose in the α and β forms and in the different isotopically substituted forms. The validity of the potential energy constants developed in this fit was tested by predicting the spectra of α and β mannose and α and β galactose. On the basis of the quality of the fit it was possible to predict the spectra of the two forms of mannose and two forms of galactose with almost the same accuracy as that of the fit to the spectra of the various forms of glucose. Furthermore, it was possible to distinguish the most probable form of the rotamers about C-6 in the compounds for which crystal data were not available.

The Inositols

The next in the series of model compounds was the class of the inositols studied by R. Williams; these are the cyclohexane hexols, which have the same number of internal degrees of freedom as the hexoses, but the diversity of types of chemical bonds is far less than in any of the preceding classes investigated. The inositols have often been used as model compounds to explore conformational effects in carbohydrates. These might logically have been the group of compounds to begin with in the present work, except that the acquisition of samples of a sufficient number of the isomers took some time. The investigation was undertaken because the high degree of symmetry of some of the isomers made it possible to test far more rigorously the validity of many of the approximations and methods that had been adopted in the previous studies. In this investigation the spectra of four of the isomers were used as the basis for developing the potential energy constants and these were then used to predict the spectra of the three other isomers that were available. In both instances the quality of the fit was quite good considering that the high symmetry imposes additional constraints. This study also made possible a careful assessment of some of the mathematical procedures used in the analyses.

Ongoing Studies on Oligosaccharides

With the conclusion of the study on the inositols our investigations of the single ring compounds were completed and the foundation had been established for exploring the spectra of the disaccharides and oligosaccharides. These are currently under investigation in the thesis programs of Ken Carlson and John Gast. Carlson is investigating the spectra of the cellodextrin series with emphasis on cellobiose, and Gast is studying the xylodextrin series with emphasis on xylobiose. With acquisition by the Institute of the new NMR system, the NMR spectra, both proton and carbon-13, are being utilized to aid in understanding these molecules.

